

Enhancement of Photocatalytic Hydrogen Production by Liquid Phase Plasma Irradiation on Metal-loaded TiO₂/Carbon Nanofiber Photocatalysts

Kyong-Hwan Chung¹, Byung-Joo Kim², Kay-Hyeok An³, Young-Kwon Park⁴, Sang-Chul Jung^{1*}

¹Department of Environmental Engineering, Suncheon National University, 255 Jungang-ro, Suncheon, Jeonnam 57922, Republic of Korea

²R&D Division, Korea Institute of Carbon Convergence Technology, 110-11 Banryong-ro, Jeonju 54853, Republic of Korea

³Department of Nano & Advanced Materials Engineering, Jeonju University, 303 Cheonjam-ro, Jeonju 55069, Republic of Korea

⁴School of Environmental Engineering, University of Seoul, 163 Seoulsiripdaero, Dongdaemun-gu, Seoul 02504, Republic of Korea

*corresponding author

ABSTRACT

Hydrogen evolution by water photocatalysis using liquid phase plasma irradiation was studied on TiO₂ photocatalysts. Effect of liquid phase plasma irradiation in the reaction was evaluated. Carbon nanofiber was employed as a photocatalytic support for Ni-loaded TiO₂ photocatalyst. The rate of hydrogen evolution was increased by the metal loading on the TiO₂ surface. The carbon nanofiber was acted as useful photocatalytic support for the fixation of TiO₂. Hydrogen evolution was enhanced by the Ni loading on the TiO₂ supported onto the carbon nanofiber.

I. INTRODUCTION

Hydrogen production by photocatalysis on high photosensitive catalysts has been studied under UV and visible light irradiation [1]. In particular, visible light sensitive photocatalysts for hydrogen generation from water have attracted considerable attention [2]. Although a range of light sources have been employed in photocatalysis, few studies have examined photocatalysis for hydrogen generation using liquid phase plasma (LPP) by irradiation into water directly [3]. This study examined the hydrogen evolution by water photocatalysis using LPP on metal-loaded TiO₂ photocatalysts. The photocatalysts were supported on carbon nanofiber (CNF) support. The photocatalytic activities were estimated for hydrogen production from water. The rates of hydrogen evolution by LPP irradiation was compared with those of UV light irradiation on the same photocatalysts. Effect of sacrificial reagent added into water was also evaluated in the photocatalysis for hydrogen evolution.

II. EXPERIMENTAL

Photocatalysts. TiO₂ (P25, Degussa), consisting of anatase and rutile was used as a parent photocatalyst. Ni, Fe, and Co ions were introduced as the metal ions loaded onto the TiO₂ photocatalysts. The metal-loaded TiO₂ photocatalysts were prepared using the typical incipient wetness impregnation method. The metal ions were loaded on the TiO₂ at a 2 wt% theoretical content.

CNFs (Aldrich, >98% carbon basis, graphitized platelets) were introduced as a support for the photocatalyst in the reaction. To incorporate the TiO₂ nanocrystallites on the support, the TiO₂ sol was prepared by dissolving of titanium isopropoxide (Daejung, 99.9%) into anhydrous ethanol (Daejung, 99%). TiO₂/CNF photocatalyst were prepared by the wetness impregnation method for CNF zeolite in TiO₂ sol. CNF zeolite was soaked into a TiO₂ sol. After stirring for 4 h, the sample was calcined at 500 °C for 5 h. Nanocrystalline TiO₂ was obtained by drying and calcination at 500 °C.

Water photocatalysis by LPP irradiation. Distilled water was employed as the reactants. The TiO₂, metal-loaded TiO₂, and TiO₂/CNF were introduced as photocatalysts in the photocatalytic reaction. The amounts of reactants and photocatalysts were adjusted as 200 mL and 0.5 g, respectively. The photocatalytic reaction was

carried out for water in a completely air-free system connected to a gas chromatograph (GC). The gas products produced during the reaction were carried by a N_2 carrier gas at a continuous flow to the GC. The temperature of the LPP reactor was maintained at 25 °C with cooling water. The gas products were analyzed by GC (Younglin, M600D) equipped with a thermal conductivity detector and a molecular sieve 5A packing column. The electric discharge was generated from a needle-to-needle electrode system in a double annular tube reactor in a liquid. The plasma in the liquid reactant was generated by the plasma power supply. A bipolar pulse power supply with high frequency (Nano Technology Inc., NTI-1000W) was used to generate the pulsed electrical plasma discharge in the liquid directly.

III. RESULTS AND DISCUSSION

Characteristics of the optical emission and photocatalysts

Fig.1 presents TEM image of CNF and TiO_2 /CNF photocatalyst. The TiO_2 nanocrystallites were loaded in the CNF. This was also confirmed by Ti mapping. The loading of TiO_2 on CNF defined from EDS measurement was ca. 42 wt%. Fig.1(c) presents the DRS data of the photocatalysts expressed as Kubelka-Munk units. The optical properties of the photocatalysts were initiated by light absorption in the photochemical processes. The spectrum of TiO_2 exhibited an adsorption edge at ca. 380 nm. The DRS of $Ni-TiO_2$ /CNF was also shifted to an upper range compared to that of TiO_2 ; its adsorption edge was ca. 395 nm, which corresponds to a bandgap of 3.1 eV. With the loading of Ni atoms on TiO_2 /CNF, its DRS were shifted to a higher range compared to TiO_2 . This suggests that the photosensitivity of $Ni-TiO_2$ /CNF was improved by Ni loading.

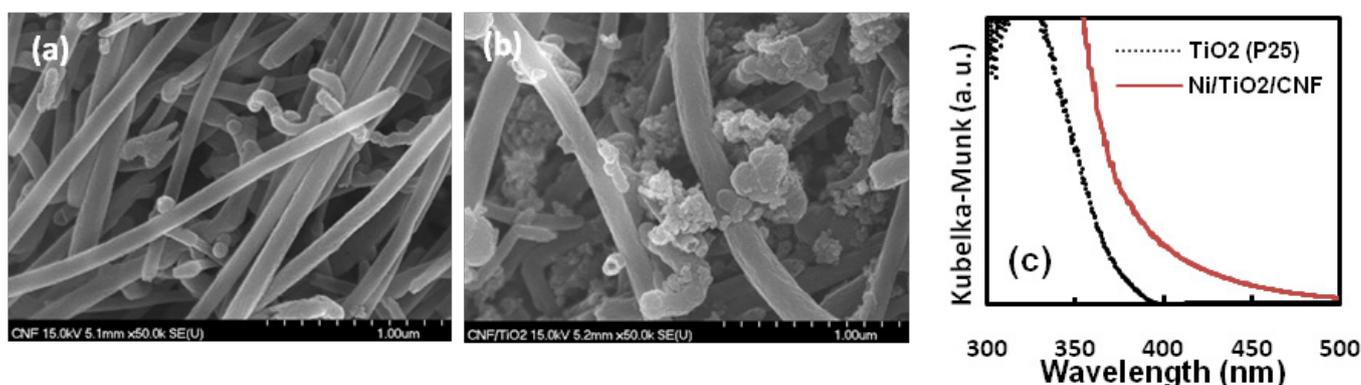


Figure 1 (a) TEM images of CNF and (b) TiO_2 /CNF photocatalysts. (c) UV-vis diffuse reflectance adsorption spectra of Ni-loaded TiO_2 on CNF support.

Hydrogen evolution by LPP irradiation. Hydrogen was obtained in the gas products with a small amount of oxygen from the photocatalysis of water. No new liquid products were obtained during the photochemical reaction. Fig. 2(a) presents the rate of hydrogen evolution from water using LPP without photocatalysts, and with TiO_2 photocatalyst addition. A small amount of hydrogen was evolved by LPP irradiation despite the lack of a photocatalyst. The rate of hydrogen evolution increased with increasing irradiation time. The amount of hydrogen production was increased significantly on the TiO_2 photocatalyst.

Fig. 2(b) presents the rate of hydrogen evolution on metal oxide photocatalysts supported on the CNF. The samples, TiO_2 and Ni/TiO_2 , supported on the CNF were adopted as 0.5 g in the photocatalysis. The amount of TiO_2 nanocrystallites incorporated on the CNF ca. 42 wt%, as defined from the TEM-EDS results. This suggests that the CNF can serve as a photocatalyst support incorporating a considerable amount of TiO_2 photocatalyst. The rate on TiO_2 supported onto the supports was slightly higher than on the TiO_2 photocatalyst. This is caused that the crystal size of TiO_2 (TS) loaded on the supports were smaller than that of pure TiO_2 (P25). On the other hand, the hydrogen evolution on $Ni-TiO_2$ /CNF was increased by the Ni loading. This result was derived from the improved in photosensitivity with the Ni loading. This is due to the extended photoresponsible range.

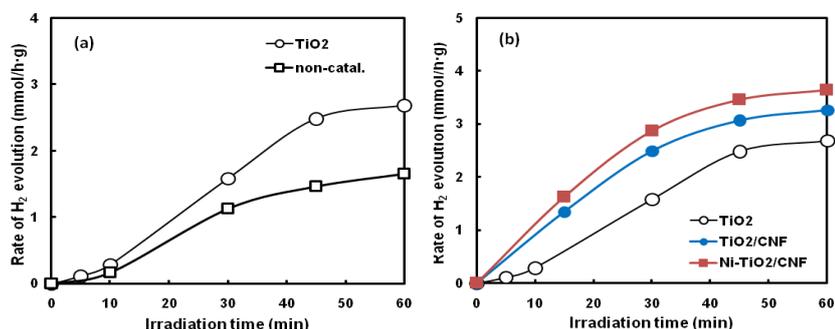


Figure 2 (a) Hydrogen evolution from water photocatalysis using LPP on various photoreaction conditions. (b) Rate of

hydrogen evolution on Ni-loaded TiO₂ and TiO₂ supported on CNF.

IV. SUMMARY

Hydrogen was produced from the photodecomposition of water by liquid phase plasma irradiation with and without photocatalysts. The rate of hydrogen evolution was increased by the metal loading on the TiO₂ surface. The carbon nanofiber was employed as a useful photocatalytic support for the fixation of TiO₂. Hydrogen evolution was enhanced by the Ni loading on the TiO₂ supported onto the carbon nanofiber support. The rate of hydrogen evolution was about 10 times higher than that in UV lamp irradiation.

V. REFERENCES

- [1] A.A. Ismail, D.W. Bahnemann, Photochemical splitting of water for hydrogen production by photocatalysis: A review. *Sol. Energy Mater. Sol. Cells* 128 (2014) 85–101.
- [2] Z. Jiefang, Z. Michael, Nanostructured materials for photocatalytic hydrogen production. *Curr. Opin. Colloid Interface Sci.* 14 (2009) 260–269.
- [3] J.S. Jang, H.G. Kim, J.S. Lee, Heterojunction semiconductors: A strategy to develop efficient photocatalytic materials for visible light water splitting. *Catal. Today* 185 (2012) 270–277.